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Study in calcium carbonate crystal formation at the air/water Interface in the presence of a magnetic field

Tim Paschke
with Anca Lungu and Frank Hunte
University of Minnesota – Magnetic Microscopy Center
Spring 2001

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Introduction

Calcium carbonate scale formation is of great interest because of its detrimental effect on many industrial processes. Scale intrudes on pipes and limits flow. It also hugely decreases heat transfer, reportedly as much as 95% for a 25mm layer of calcuim carbonate [1]. Traditionally this scale is cleaned out using mechanical or chemical methods. These are labor-intensive, costly, and often environmentally unsound. In contrast, magnetic water treatment (MWT) has been touted by its proponents as the "miracle" solution to scaling [2]. MWT can reportedly cease any additional scale from forming and, by some accounts, can even loosen existing scale enough for normal circulation to carry it away [3]. Critics of MWT claim that it has little or no effect on scaling, or any other property of water. Proponents concede that the mechanism at work is not understood, but point to numerous and varied case studies, anecdotal reports, and controlled experiments to support their claims. Unfortunately, MWT manufacturers themselves conduct large amounts of the research, making objective inquiry comparatively rare.

Aggregation processes, like those occurring inside heavily scaled pipes, can be classified into two types. Cluster-particle aggregation involves mobile particles fixing onto a stationary cluster. Cluster-cluster aggregation (CCA) involves two or more clusters moving together and sticking [4]. This study examines the latter case, CCA of calcium carbonate at a stationary air/water interface. For many proposed applications of MWT, the fluid to be treated flows past the magnet. The magnets can either be integrated into the circulation loop or fixed externally [4]. In any case, the motion of fluid past the magnet introduces additional variables not present in a static system. This study attempts to remove any factors involving the flow of fluid through the field.

At the air/water interface calcium carbonate commonly grows as calcite [5]. Calcite crystals are rhombohedral, and form a hard, tenacious scale [6]. The other common form of $CaCO_3$ is aragonite. Aragonite crystals are needle-like, while calcite is equiaxed. We gauge the growth of the calcium carbonate by recording the fractal dimension of the crystal structure over time. It is reasonable to assume that problematic calcite crystals would form in a more complex fractal pattern than acicular aragonite. For similar growth patterns, the fractal dimension gives an idea of the comparative speed of aggregation.

Nakayama et al. studied the growth of calcite with this method in zero field. They report fractal dimension $D_f \sim 1.46\text{-}1.49$, corresponding to the "fast" aggregation condition. This is diffusion-limited CCA, in contrast to reaction-limited "slow" aggregation. Fast aggregation occurs as fast as particle diffuse close enough to aggregate, while slow aggregation is limited by the speed of the crystallization reaction.

Experimental Procedures

When an aqueous solution of calcium hydroxide ($Ca(OH)_2$) is exposed to the air small particles of calcium carbonate form at the interface by reacting with carbon dioxide. The reaction is described by:

$$CO_2 + H_2O \rightarrow H_2CO_3$$
$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O$$

We used $Ca(OH)_2$ at a concentration of 0.30 mg/L. It was stored in 500 mL Nalgene bottles and aged 6-12 months. We completely covered the bottom of a 35mm petri dish with solution (approximately 2.5 mL.). All experiments were carried out at room temperature. We collected the data using a PC and CCD camera. The camera had a Navitar 7000 lens with 6x magnification, and our PC used a frame grabber video capture board (National Instruments IMAQ.) The CCD camera had a resolution of 640x480 pixels. For our images, one pixel corresponds to about 10μm. We took grayscale photos at approximately 5-minute intervals for 120 minutes. Data were collected for 12 individual runs at 5 field conditions. We studied growth in zero field, 1 kG and 10 kG field parallel to the interface, and 4 kG perpendicular to the interface. We also studied growth at approximately 7 kG and high gradient (maximum force) parallel to the interface. For the parallel field we used an electromagnet. Shown below is the profile for the parallel field at maximum strength.

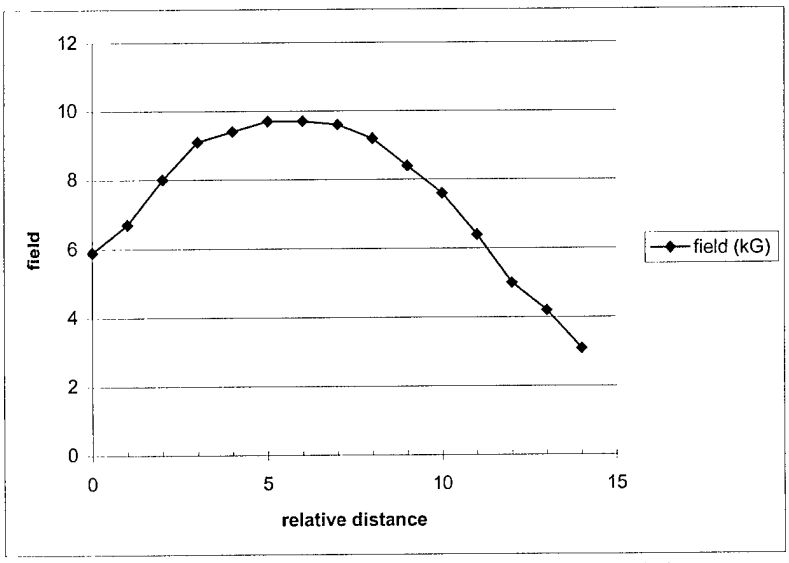


Fig 1:Field profile for ring magnet at 10 kG (parallel orientation)

This magnet yielded maximum gradient of 1.2 kG/cm. We took data at the point of maximum gradient times field, in this case about 9.6 kG*kG/cm.

For the perpendicular field we used a permanent NdFeB magnet. A 2-D field profile for this magnet at the sample elevation is shown in figure 2. The sample was placed within a 35mm diameter ring centered on the field maximum, and the crystals grew within a concentric 15 mm diameter cicle.

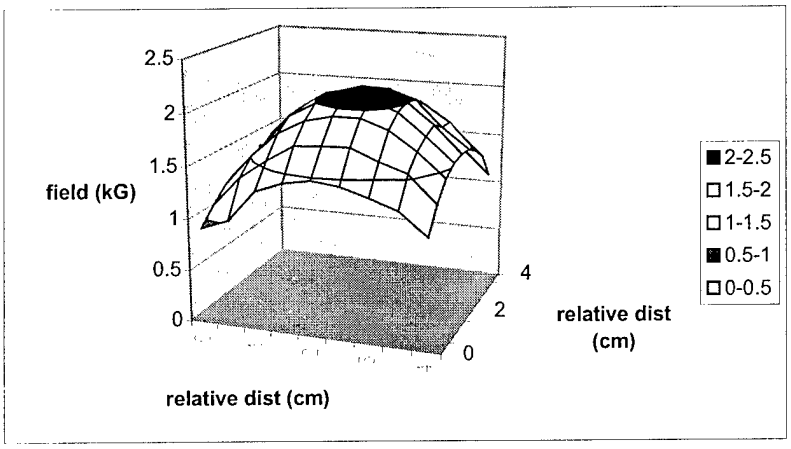


Fig 2: Field profile for NdFeB magnet (perpendicular orientation)

Experimental Results

Within 10 minutes of filling the petri dish small particles of calcite were visible. These particles float at the interface due to surface tension [4]. Because of convection they collide with other particles to form larger crystals. These crystals drift on the interface, sometimes slowly turning and colliding with other crystals. Nakayama et al. noticed the larger crystals sticking at one point, then rotating until they contacted at another point and stuck again [4]. We also noticed this tendency, resulting in inner loops forming across the crystal aggregate.

The large cluster motion was primarily caused by two factors. First, convection within the solution and air currents moved the crystals, more or less randomly back and forth. Second, the air/water interface seemed to be somewhat bowl-shaped. This was apparently caused by interaction at the edges of the petri dish. The solution appeared to wet the dish, clinging to the edge. For all trials, and in all conditions, the initial crystals appeared in uniformly disperse pattern. As the crystals grew larger, they were slowly pulled down into the center of the dish, the bottom of the bowl. The structures at the perimeter moved fastest, combining with the structures adjacent towards the center. Because of this, as the aggregate grew it was always more dense with crystal structure (loops and fingers) at its perimeter than at the center.

One other factor influenced crystal motion at the maximum force condition. In all trials, the crystals were pulled into the region of higher field. The single crystalites were uniformly distributed as they appeared, then were pulled into the field as they grew and

aggregated. It was made more apparent that the interface was bowl-shaped when the field was switched on and off after the experiment was concluded. The crystals would always migrate into the region of higher field, assuming an oval shape and displacing into the field by about 7 mm in 10 minutes. When the field was switched off, they would revert back to a circular shape in the center of the dish. Repeatedly switching the field yielded the same results.

Crystals for all trials were qualitatively similar. The crystal structure was branched and interconnected, with many small loops approximately 100-200 μm across. Within 70-80 minutes the growth ceased, suggesting that the Ca in the solution had been exhausted. The final crystal conglomerate was approximately 15 mm in diameter.

As the first step in reducing the data we used the threshold function on Adobe PhotoShop 5.0 to render the image in black and white. The crystals were shown in white, and the surrounding solution in black. Shown in figure 1 are two versions of the same photo, the original in grayscale and the processed in black and white.

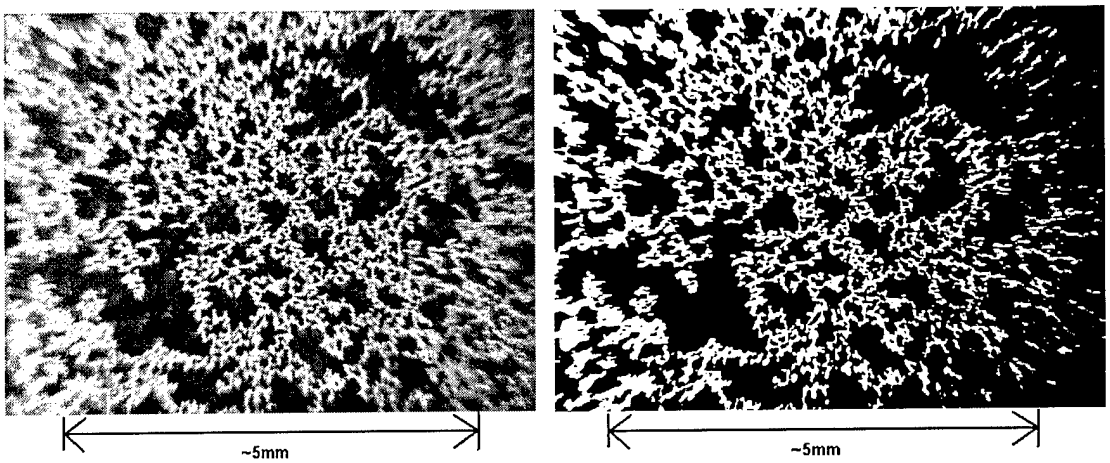


Fig. 1: Original and threshold image

Next we cropped off the edges of each photo, yielding a final black and white image approximately 380x270 pixels. This was necessary because the lens's finite depth of field caused distortion at the edges of the photo. This distortion made the crystals irresolvable outside the cropped region. This is apparent in the photos above. The final black and white, cropped photo was analyzed using software called Benoit ver. 1.3 by Fractal Analysis Software. We recorded the fractal dimension using the box-counting method for each photo. Figure 2 below is a cropped image ready for final processing.

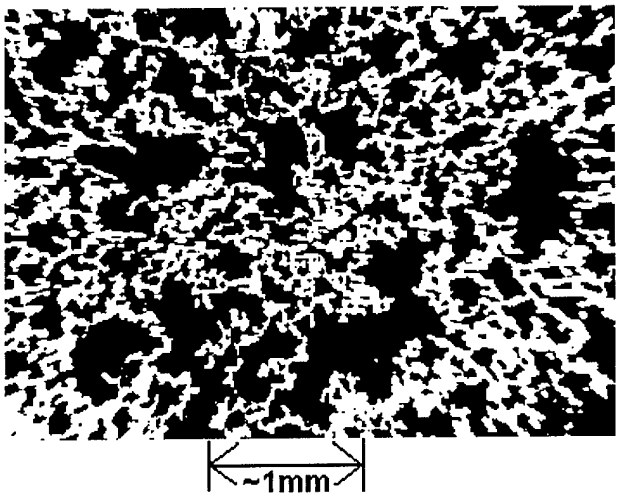
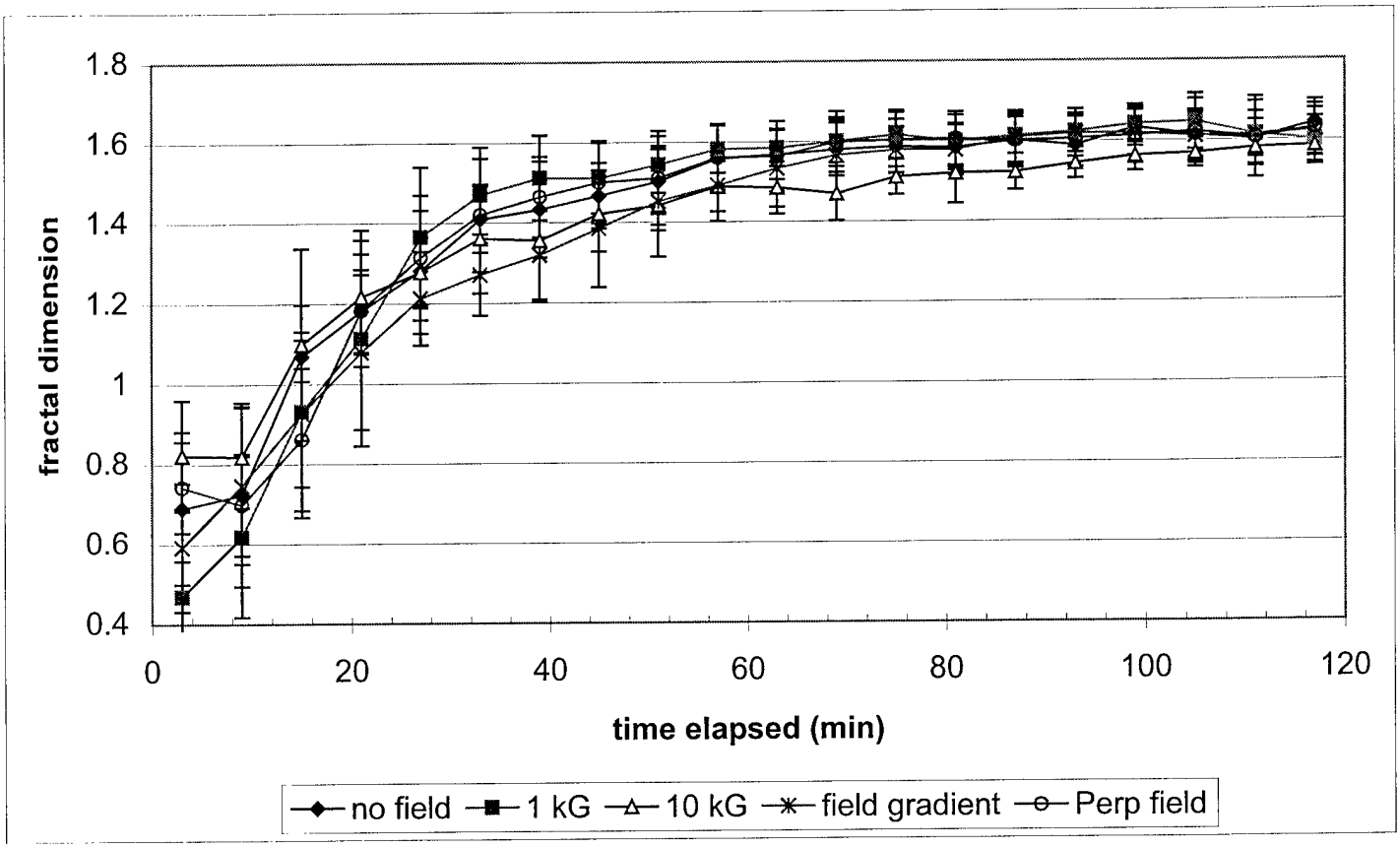


Fig. 2:Cropped threshold image

The results of all twelve runs were compiled into one set of data, and organized into 6-minute bins. We plotted the average fractal dimension for the 6-minute periods for each condition. Our final results are shown in the following graph.



Graph 1: D_f for all trials

The fractal dimension reaches a nearly constant value after 80 min have elapsed. Table 1 shows the average fractal dimension for all data gathered after 80 min.

	Ave. D_f	Std. Dev.
No field	1.61	0.05
1 kG	1.63	0.06
10 kG	1.56	0.05
Field gradient	1.61	0.06
Perpendicular field	1.61	0.07

Table 1: D_f after 80 min

Conclusions

Our data indicate that for all conditions fractal dimension increases over time, reaching its maximum value by 80 minutes and then remaining constant. In contrast to Nakayama, we see a fractal dimension closer to 1.6, higher than any reported "fast" or "slow" CCA processes [4]. Fractal dimensions for our processes are closer to diffusion-limited aggregation (DLA), the growth of stationary crystals from the diffusion of small mobile particles. Simulations for "perfect" DLA give $D_f = 1.6 \pm 0.01$ [8]. It seems there may be an effect on fractal dimension for the 10 kG parallel field. The data are suggestive but far from conclusive. Final fractal dimension in 10 kG is about 0.05 lower than all other conditions; never more than one standard deviation different from the other four conditions, but consistently less than all of them.

Nakayama studied varying concentrations of $Ca(OH)_2$ and noticed the fractal dimension had very little dependence on concentration [4]. Our trials used common solution for many runs, spanning a large time period. It is reasonable to conclude that as this solution was exposed to the air when the bottle was opened, calcite slowly precipitated in the bottle just as it did in our experiments. This effectively reduced the solution's concentration of $Ca(OH)_2$. We noticed no change in fractal dimension for most of the solution's lifetime, supporting Nakayama's results. However, there seemed to exist a critical concentration, below which crystals would not form. For one or two trials, the crystals would be noticeably smaller and grow slower. Then, catastrophically, the crystals would not grow at all. If the threshold were reached during a particular set of trials, the entire set would be performed again with unopened solution.

We also gathered qualitative data from growth in 8T, but it could not be processed in the same way as the other data. There appeared to be no difference in growth patterns or speed, but additional research should be done to confirm this assessment.

Discussions

Most articles claiming the efficacy of MWT are published by product manufacturers. These results must therefore be immediately suspect. Despite this, some controlled experiments carried out independently have shown promising results. Dalas and

Koutsoukos show a "strong retardation on the crystallization of calcite" for certain fields, but only at intensities exceeding 10 T [8].

Coey and Cass used commercially available MWT devices to treat Irish well water and commercial mineral water. They heated it to produce limescale, and analyzed the ratio of aragonite to calcite in the scale. Aragonite has orthorhombic crystal structure and is less likely to form scale than calcite. Coey and Cass claim it is 99.9% probable that the MWT they studied increased the ratio of aragonite to calcite [6].

Some of the more inquisitive researchers have proposed possible mechanisms for the reported effects [1, 3, 6]. Nafalski et al. propose that the presence of a magnetic field may have one or more of the following effects:

1) Alteration of the motion of ions or colloidal particles through the Lorentz force. In our experiment, the only motion of ions or particles through the field was due to convection. In all MWT devices, flow past the magnet is a necessary part of the system.

2) Electrochemical corrosion phenomena as a result of Faraday's effect. The corrosion results in ferric and ferrous species in the water. Oxidized iron can be produced from the housing, which then acts as a nucleation center for precipitation. The $Ca(OH)_2$ used to make our solution already had iron present at 0.05%. Faraday's effect is also a result of motion through the magnetic field, so it would not likely have played a significant role in any effect observed.

3) Phenomena related soley to ferric and ferrous species in the treated water. Nafalski reports that trace ferrous ions can strongly inhibit calcite growth, but not aragonite. They can also inhibit the transformation of aragonite into calcite.

Coey and Cass have two unique ideas to explain the positive result they observed. First, the field might "lower the energy of a nucleus because of a difference in susceptibility with the surroundings." Since their analyses did not find Fe or Mn in the aragonite crystals, this effect seemed too weak to account for their result. Second, the field may "influence clusters of iron or manganese hydroxide that act as heterogeneous nucleation centers" [6]. This effect may be coupled to iron hydroxide produced from Faraday's effect.

Our experiments show static magnetic field has no effect on the fractal dimension or the growth rate of calcite crystals. As Coey suggests, further well-defined experiments may help determine which mechanism is at work. More experiments with ultra-pure calcium carbonate solutions, experiments involving static and varying magnetic fields, and varying speeds of flow and magnetic field exposure time may help eliminate many of the possible mechanisms. The commercial benefits suggested, as well as the scientific edification to be reaped, make further research into MWT and magnetic effects on crystallization a necessity.

References

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